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**UNITED STATES PATENT APPLICATION**

of

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for new and useful invention entitled:

**NARROW ENERGY BAND GAP GALLIUM ARSENIDE NITRIDE  
SEMI-CONDUCTORS AND AN ION-CUT-SYNTHESIS METHOD FOR  
PRODUCING THE SAME**

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**NARROW ENERGY BAND GAP GALLIUM ARSENIDE NITRIDE  
SEMI-CONDUCTORS AND AN ION-CUT-SYNTHESIS METHOD FOR  
PRODUCING THE SAME**

**CROSS REFERENCE TO RELATED APPLICATION**

[0001] This application claims priority based on U.S. Provisional Patent Application No. 60/425,388, filed November 12, 2002, which is hereby incorporated by reference in full.

**STATEMENT REGARDING FEDERALLY SPONSORED  
RESEARCH OR DEVELOPMENT**

[0002] This invention was made with government support of grant #ACQ-1-30619-14 from National Renewable Energy Laboratory and grant #F49620-00-1-0328 from Air Force Office of Scientific Research. The government has certain rights in the invention.

**FIELD OF THE INVENTION**

[0003] The present invention generally relates to a gallium arsenide based semi-conductor material, and more particularly, the present invention relates to a gallium arsenide nitride semi-conductor with a narrow energy band gap.

**BACKGROUND OF THE INVENTION**

[0004] Gallium alloys have been shown to exhibit a reduced energy band gap that fluctuates as a function of the amount of arsenide and nitride added thereto. For example, 1% atomic nitrogen added to gallium arsenide (GaAs) to form gallium arsenide nitride (GaAsN) has been shown to reduce the energy band gap by as much as 200 meV. Likewise, the introduction of 1% arsenic into gallium nitride (GaN) to form GaAsN has been shown to reduce the band gap by as much as 700 meV. The resulting material is applicable and useful in a wide range of semi-conductor

applications. Specifically, narrow energy band gap semi-conductors constructed with such alloys are useful in long wave length light emitters and detectors, high performance electronic devices, and high efficiency solar cells.

[0005] Many conventional methods of GaAsN formation in the semi-conductor industry involve an epitaxial or other similar growth process, molecular beam epitaxy (MBE), gas-source MBE (GS-MBE), metalorganic chemical vapor deposition (MOCVD) and sputtering. While these methods do result in the formation of GaAsN material applicable for semi-conductor usage, growth processes place a solubility limit on the amounts of nitrogen that can be contained within the resulting GaAsN material.

[0006] Other methods, such as that disclosed in the article entitled, "High Concentration Nitrogen Ion Doping Into GaAs For The Fabrication Of GaAsN," reported in the publication *Nuclear Instruments And Methods In Physics Research* B 118 (1996) 743-747, discloses other methods of doping GaAs with nitrogen, which do achieve better solubility of nitrogen into the GaAs material. Specifically, nitrogen ions are implanted into a LEC formed GaAs substrate by high energy (400 keV) ion implantation. This process is then followed by an annealing process.

[0007] While this approach provides a means for doping GaAs with nitrogen, there is a desire to improve manufacturing methods of forming such substrates. Such desire is to conserve material and decrease the size of the GaAsN layer, as well as the underlying substrate to only the size that is needed for an application.

### **SUMMARY OF THE INVENTION**

[0008] The present invention provides a Nitrogen implanted Gallium material with improved optical and luminescent characteristics, and an ion-cut-synthesis method to accomplish the same.

[0009] Other aspects of the invention will be apparent to those skilled in the art after reviewing the drawings and the detailed description below.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0010] The present invention will now be described, by way of example, with reference to the accompanying drawings, in which:

[0011] **FIG. 1** is a schematic view illustration of a semi-conductor material according to the present invention;

[0012] **FIG. 2a** is a TEM picture of semi-conductor material according to the present invention;

[0013] **FIG. 2b** is a TEM picture of semi-conductor material according to the present invention;

[0014] **FIG. 2c** is a TEM picture of semi-conductor material according to the present invention;

[0015] **FIG. 3** is a graphical view illustration of a photoluminescence data from semi-conductor material according to the present invention;

[0016] **FIG. 4a** is a schematic view illustration of a manufacture of semi-conductor material according to the present invention;

[0017] **FIG. 4b** is a schematic view illustration of a manufacture of semi-conductor material according to the present invention;

[0018] **FIG. 4c** is a schematic view illustration of a manufacture of semi-conductor material according to the present invention;

[0019] **FIG. 4d** is a schematic view illustration of a manufacture of semi-conductor material according to the present invention; and

[0020] **FIG. 5** is a plot of a simulation of a retained dosage of nitrogen and penetration depth of semi-conductor material according to the present invention.

**DETAILED DESCRIPTION OF THE EMBODIMENTS**

[0021] The present invention improves the methods for forming GaAsN substrates by providing a means for creating a GaAsN layer that includes ion implantation into a different GaAs substrate, than that which is to be used for the resulting low energy band gap application. This implantation causes a GaAsN layer to be formed to a depth in the GaAs substrate based on implanting characteristics of the implantation process. The implantation also forms microbubbles that separate the GaAsN layer from the remainder of the GaAs substrate. The GaAs substrate can then be attached to another substrate for use in a reduced energy band gap application. By this way, only a minimum needed layer can be created in the GaAs substrate, leaving the remainder of the substrate for other uses. The receiver substrate can also be specifically sized for the desired application as the exact depth of the GaAsN layer is known.

[0022] Referring now to FIG. 1, a semi-conductor material 10 is shown as having a thin film 12b including a GaAs matrix 16 and GaAsN nanostructures 18 positioned therein. Thin film 12b is disposed on substrate 14 that is composed of a base material such as GaAs, silicon or other suitable material. Thin film 12b is preferably initially 0.15  $\mu\text{m}$  in thickness. However, it is noted that other thicknesses are possible, and that the present invention is not limited to that disclosed herein.

[0023] FIG. 2 shows dark-field diffraction contrast TEM images of 750 (FIG. 2a), 800 (FIG. 2b) and 850°C (FIG. 2c) annealed samples of thin film 12b. It should be noted that the images of thin film 12b as shown in FIG. 2 are attached to substrate 15 (See FIG. 4). However, for purposes of description, the structure of thin film 12b as described with reference to FIG. 2, is applicable to the thin film 12b of both FIGs. 1 and 4. The ion-cut-synthesis method used to effectuate the transfer of thin film 12b

from substrate 15 to substrate 14, will be described in greater detail in the following sections.

[0024] In FIG. 2, three regions are shown including a surface layer 1, a 150-nm-thick middle layer 2, and a near-substrate layer 3. It is noted that although specific dimensions are shown and described, other variations to the depth and composition of the layers are possible dependent upon the nitrogen implantation and annealing characteristics as described hereinafter. For the thin film 12b shown in FIGS. 2a, 2b, and 2c, the middle layers preferably contain 2-10 nm sized GaAsN nanocrystallites in an amorphous GaAs matrix.

[0025] Referring now to FIG. 3, a photoluminescence spectroscopy plot is provided depicting the intensity and wavelength optical properties of thin film 12b as shown and described. The intensity is in arbitrary units while the wave length is in nanometers. The un-implanted state illustrates the wavelength and photoluminescence scenario where a GaAs material is not combined with nitrogen. Here, it can be seen that the photoluminescence has a high intensity between wavelengths of about 800 to 850 nm. When nitrogen is implanted and the thin film is annealed at temperatures of 750°C, 800°C and 850°C, respectively, it can be seen that a photoluminescence intensity increase is achieved between the wavelengths of about 900 and 1050 nm.

[0026] Referring now to FIGS. 4a-4d, an ion-cut-synthesis method for preparing the semi-conductor material according to the present invention is shown and described. In FIG. 4a, a GaAs substrate 15 is grown by VGF or other suitable methods and similar techniques. A base film 12 is then grown thereon by molecular beam epitaxy or other similar techniques such as MOCVD or GS-MBE. Preferably,

the GaAs base film 12 is grown to a depth of 1.5  $\mu\text{m}$  above the upper surface of the substrate 15 and formed as a uniform and stoichiometric matrix.

[0027] With continued reference to FIG. 4a, nitrogen ions are implanted into the thin film 12 by a high energy ion implantation method. In the preferred embodiment of the present invention, the nitrogen is implanted in base layer 12 by maintaining the base film 12 at a temperature of 300°C and implanting nitrogen at a concentration of  $5 \times 10^{17} \text{cm}^{-2}$  by a high energy (100keV) ion implantation. The retained dose from this implantation is preferably about  $1.7 \times 10^{22} \text{N/cm}^3$  at a depth of .15  $\mu\text{m}$  into the base film 12. However, as will be understood by one skilled in the art from reviewing FIG. 5, modifications and variations of this retained dosage and implantation depth can be obtained. In the preferred embodiment of the present invention, it is desirable to obtain both a sufficient depth, as well as a high retained dosage of nitrogen in the base film 12 to form the thin film 12b. As can be seen, the implantation depth of the nitrogen ions preferably falls far short of the depth of the grown thin film 12b to allow reusability of the base film 12 for forming multiple thin films 12b. As a result, only the upper portion of the base film 12 is used for formation of thin film 12b.

[0028] Referring now to FIG. 4b, implanted portion 12b is affixed to substrate 14 by wafer bonding technology. Substrate 14 can be GaAs, silicon, or other suitable material. As shown in FIG. 4c, substrate 14, thin film 12b and substrate 15 are then annealed at a temperature between 750 and 850°C, as described in FIG.4. The time for annealing is preferably 30 seconds. The annealing process results in the formation of the GaAsN nanostructures 18 (see FIG. 1) to create the desired photoluminescence at longer wavelengths as described with reference to FIG. 3. Additionally, the annealing process causes the formation of nitrogen microbubbles 22 that causes separation of the thin film 12b from the remainder of base layer 12 or unimplanted

portion 12a. The microblister formation occurs at the preferred implantation depth of .15  $\mu\text{m}$  and thereby causes cleavage of the implanted portion 12b from the unimplanted portion 12a. Referring to FIG. 4d, the implanted portion 12b containing GaAsN is cleaved from unimplanted portion 12a, thereby leaving a damaged layer 12c. Implanted portion 12b is then polished, as known to one skilled in the art, to create a resulting semi-conductor material 15 that includes substrate 14 and implanted GaAsN portion 12b. The material is then used in known semi-conductor manufacturing processes to form the desired components which include, but are not limited to, long wave length light emitters and detectors, high performance electronic devices, and high efficiency solar cells. As the implantation depth includes only a small upper portion of thin film 12, the damage layer 12c can be removed by polishing to leave the remaining unimplanted portion 12a. As only the upper layer of base film 12 is used, the remaining portion 12a can then be used to form additional thin films 12b for further applications.

[0029] While the present invention has been particularly shown and described with reference to the foregoing preferred and alternative embodiments, it should be understood by those skilled in the art that various alternatives to the embodiments of the invention described herein may be employed in practicing the invention without departing from the spirit and scope of the invention as defined in the following claims. It is intended that the following claims define the scope of the invention and that the method and apparatus within the scope of these claims and their equivalents be covered thereby. This description of the invention should be understood to include all novel and non-obvious combinations of elements described herein, and claims may be presented in this or a later application to any novel and non-obvious combination of these elements. The foregoing embodiments are illustrative, and no single feature



or element is essential to all possible combinations that may be claimed in this or a later application. Where the claims recite “a” or “a first” element of the equivalent thereof, such claims should be understood to include incorporation of one or more such elements, neither requiring nor excluding two or more such elements.